Eur. Phys. J. Plus (2016) **131**: 429
DOI 10.1140/epjp/i2016-16429-3

THE EUROPEAN PHYSICAL JOURNAL PLUS

Regular Article

Construction of the energy matrix for complex atoms

Part VI: Core polarization effects

Magdalena Elantkowska[1,a], Jarosław Ruczkowski[2], and Jerzy Dembczyński[2]

[1] Institute of Materials Research and Quantum Engineering, Faculty of Technical Physics, Poznan University of Technology, Piotrowo 3, 60-965 Poznań, Poland
[2] Institute of Control and Information Engineering, Faculty of Electrical Engineering, Poznan University of Technology, Piotrowo 3A, 60-965 Poznań, Poland

Received: 3 October 2016
Published online: 15 December 2016

Abstract. The continuation of series of papers concerning the construction of the energy matrix for complex atoms is presented. The second-order perturbation theory contributions originating from core polarization effects in the hyperfine structure are considered. Fifteen new formulae for angular coefficients of core polarization parameters are given. The complete set of corrections up to the second-order perturbation theory was taken into account and the accuracy of the wave functions in the intermediate coupling scheme, on the example of the lanthanum atom, was checked.

1 Introduction

In the first part of our series of publications entitled *Construction of the energy matrix for complex atoms*, a method of semi-empirical analysis of complex atoms was introduced in general [1]. In the subsequent works of this series, an exhaustive description of electrostatic interaction up to second-order perturbation theory, electrostatically correlated spin-orbit interactions (CSO) and electrostatically correlated hyperfine structure interactions (CHFS) was presented [2–5]. In each of these publications, the explicit form of analytical formulae, derived in our research group, was given.

The aim of this paper is a description of the effects of configuration interaction on the atomic hyperfine structure, known as core polarization effects, in the case of nl^N, $nl^N n_1 l_1^{N_1}$ and $nl^N n_1 l_1^{N_1} n_2 l_2^{N_2}$ configurations.

Important differences appear in our approach compared to previous works on the effects of configuration interactions by other authors [6–19] and can be summarized as follows:

- we replace the description of the configuration interaction with effective operators through direct expressions for matrix elements;
- we expand the considered configuration base from $nl^N + nl^{N-1} n_1 l_1$ to $nl^N + nl^{N-N_1} n_1 l_1^{N_1} + nl^{N-N_1-N_2} n_1 l_1^{N_1} n_2 l_2^{N_2}$;
- we include in the consideration the interactions between the configurations under study.

The next section of the current paper contains a short summary of the studies on the hyperfine structure of free atoms. Section 3 contains the description of a hyperfine structure many-body parametrization method. Section 4 contains the explanation of the symbols used in this work and fifteen explicit formulae for electrostatically correlated hyperfine interactions. An example of the application of new parameters for the multi-configurations system of the lanthanum atom is presented in sect. 5.

2 Effects of configuration interaction on atomic hyperfine structure

The hyperfine structure of the atomic spectra is usually interpreted in the framework of the effective operator formalism proposed by Sandars and Beck [20]. This theory assumes three radial parameters for each open shell and for each kind of multipole interaction, which should be handled as free adjustable parameters to take into account relativistic and

[a] e-mail: magdalena.elantkowska@put.poznan.pl

configuration interaction (CI) effects. The influence of CI on the hyperfine structure has been studied theoretically, especially by Judd [21, 22].

For the first time, Bauche and Judd [23] showed, in the hyperfine structure analysis of atomic plutonium, the need to consider the effects of perturbation hyperfine structure through the interaction with the configurations arising from excitation of one electron belonging to a closed shell n_0s_0 to an empty shell $n'''s'''$. The authors introduced the name of the effect as "hfs core-polarization effect".

In the following years, the extensive research on the configuration interaction effects originated from closed shells to empty shells excitations, were conducted by Judd [21, 22], Sandars [24], Bauche-Arnould [25, 26], Armstrong [27], Lindgren and Rosen [28] and Büttgenbach [29]. A short summary of these works was presented in our previous works [1, 5, 30].

In 1985, Dembczyński [31] proposed a new method of hyperfine structure parametrization, which took into consideration simultaneously one- and two-body interactions in $(3d+4s)^{N+2}$ configurations system. This approach was applied successfully to the interpretation of the spectra of iron-group elements [32–35] and, after the generalization, to the elements with three open electronic shells [36–38]. Detailed discussion on the interpretation of accurate measurements of hyperfine structure splittings in neutral and singly ionised complex atoms was presented in our papers [39, 40].

Another problem that should be considered in the interpretation of hyperfine structure is the inclusion of the off-diagonal excitation between configurations. For the first time, in the paper from 1977, Bauche and Bauche-Arnould [41] have shown that the far configuration mixing effect perturbs strongly the off-diagonal spin-dipole hfs matrix elements between $3d^{N+1}4s$ and $3d^N4s^2$ in the case of $(3d^N4s^2)^3$F Ti I and $(3d^N4s^2)^2$D Sc I. Empirically this effect has been found to be significant only by Himmel [42] in the case of OsI $5d^66s^2$. Usually the hyperfine interaction between configurations is neglected, because at first order, the only contribution to the magnetic hfs operator is due to the spin-dipole part. By Hartree-Fock calculations very small values are found for the corresponding radial integrals ($\sim \langle 4s|r^{-3}|3d\rangle$).

In 1981 Dembczyński *et al.* [43], using the atomic beam magnetic resonance detected by the laser-induced resonance fluorescence method (ABMR-LIRF), found experimental evidence of an extremely strong far configuration mixing effect on off-diagonal matrix elements between configurations, which can be explained only by taking into account the two-body core polarization effect, which screens the ordinary one-body core polarization parameter a^{10}_{3d}. Moreover, they showed that the influence of the off-diagonal spin-dipole part a^{12}_{3d4s}, which was discussed by Bauche-Arnoult, was insignificant. Later, Dembczyński presented the appropriate formulae for off-diagonal matrix elements in the case $(3d + 4s)^{N+2}$ configuration system [31].

3 Parametrization of the configuration interaction effects on the hyperfine structure

In 2010 [30] we published a new approach to the hyperfine structure many-body parametrization. In the configuration system $(5d + 6s)^N$ of the lanthanum atom, we conducted an alternative analysis of the second-order contributions, based on two excitation models: either "open shell - empty shell" or "closed shell - open shell". As a conclusion of this work, the question about the selection of the model of excitation was raised.

Computer codes for the analysis of experimental, fine and hyperfine structure, data have been developed in our research group for many years. This allowed us to conclude that consideration of excitations of one or more electrons from closed to open shells gives a more precise description of configuration interactions. Our findings can be summarized as follows:

- We suggest considering the broadest possible configurations basis in the first order of the perturbation theory, which means systems composed of many Rydberg configurations; therefore, a part of excitations from an open shell to an empty shells are included directly.
- For atoms with open 3d- or 4f-shell, additionally, the excitation from 3d (or 4f) open shell to empty shells have to be considered.
- For the configurations up to three open electronic shells, some excitations from a closed shell to an empty shell should be included; for example in lanthanum configurations $n_0s^25d^3$, $n_0s^25d^26s$, $n_0s^25d6s^2$, $n_0s^25d6s7s$, $n_0s^25d6s6d$ closed, open and empty shells are different.

The consideration of excitations of the kind "closed n_0l_0 shell-open nl shell" of the configuration with three open shells, where the second and third shells contain up to three electrons, requires the coupling of five or more angular momenta and makes calculating the angular coefficients of appropriate operators more complicated. Thus, one may expect that a precise definition and development of a sophisticated mathematical formalism provides with sufficient accuracy of determination of eigenvectors amplitudes describing particular electron states and a complete description of hyperfine configuration effects.

The theoretical description of all the possible contributions originating from the second-order perturbation theory to the atomic structure, a detailed description of the new radial parameters and the relationships between them, and also the results obtained on the basis of experimental data have been fully described in our work from 2010 [30].

However, the mathematical expressions used in the construction of the energy matrix were not given. Therefore, this paper contains analytical formulae for electrostatically correlated hyperfine interactions of the configuration space $(nl + n_1l_1)^{N+2}$.

If we consider the many configurations system, the core polarization effect should be taken into account for each type of configuration. Therefore, the next section contains the explicit formulae describing the core polarization effect for the electronic systems composed of configurations including up to three open shells (nl^N, $nl^N n_1 l_1^{N_1}$, $nl^N n_1 l_1^{N_1} n_2 l_2^{N_2}$).

4 Explicit formulae for electrostatically correlated hyperfine interactions. Excitation of one electron from a closed shell into an empty or an open shell

Explanation of symbols used and considerations on the method of the reduced matrix elements calculation have already been presented in earlier works, but for the reader's convenience, we present them again.

4.1 Explanation of used symbols

In all the formulae given below, symbol $\mathbf{G}^t$ denotes a particular term of the Coulomb interaction represented by irreducible tensors of rank t: $\sum_{i>j} r_<^t/r_>^{t+1}(\mathbf{C}_i^t \cdot \mathbf{C}_j^t)$, where $r_<$ and $r_>$ indicate the distances from the nucleus to the closer and more distant electron, respectively. Summation over t is omitted. The expressions describing $\mathbf{G}^t$ element contain coupling schemes used for the derivation of the formula.

For nj-coefficients the generally accepted notations were used.

The antisymmetric states for N equivalent electrons, allowed by the Pauli principle, were constructed from a linear combination of products of parent states with $(N-1)$ electrons using Racah's coefficients of fractional parentage [44,45]. In the one-electron fractional parentage coefficient $(nl^N \alpha_0 S_0 L_0 \{|nl^{N-1} \bar{\alpha} \bar{S} \bar{L})$, $\alpha_0 S_0 L_0$ denote the states of a group nl^N of equivalent electrons and α_0 is an additional quantum number introduced to distinguish terms with identical values of $S_0 L_0$. In the same way, $\bar{\alpha}\bar{S}\bar{L}$ denote the states of nl^{N-1} equivalent electrons. For two-electron coefficients, introduced for the first time by Donlan [46] $(nl^N \alpha_0 S_0 L_0 \{|nl^{N-2} \bar{\alpha}\bar{S}\bar{L}, nl^2 \hat{\alpha}\hat{S}\hat{L})$, $\alpha_0 S_0 L_0$, $\bar{\alpha}\bar{S}\bar{L}$ and $\hat{\alpha}\hat{S}\hat{L}$ indicate the states of a group nl^N, nl^{N-2} and nl^2 of equivalent electrons, respectively.

The expression $[x, y]$ represents $(2x + 1)(2y + 1)$. The reduced matrix elements, $\mathbf{C}^t$ and $\mathbf{U}^t$, represent

$$(l_1 \| \mathbf{C}^t \| l_2) = (-1)^{l_1} \left[(2l_1 + 1)(2l_2 + 1)\right]^{1/2} \begin{pmatrix} l_1 & t & l_2 \\ 0 & 0 & 0 \end{pmatrix} \tag{1}$$

$$\begin{aligned} &\left\langle nl^N \alpha_0 S_0 L_0 \left\| \mathbf{U}^t \right\| nl^N \alpha_0' S_0' L_0' \right\rangle = \delta(S_0, S_0')\ N\ (-1)^{L_0 + l + t}\ [L_0, L_0']^{1/2} \\ &\times \sum_{\bar{\alpha}\bar{S}\bar{L}} (-1)^{\bar{L}} \left(nl^N \alpha_0 S_0 L_0 \{|nl^{N-1} \bar{\alpha}\bar{S}\bar{L}\right) \left(nl^N \alpha_0' S_0' L_0' \{|nl^{N-1} \bar{\alpha}\bar{S}\bar{L}\right) \begin{Bmatrix} l & l & t \\ L_0 & L_0' & \bar{L} \end{Bmatrix}. \end{aligned} \tag{2}$$

4.2 Removal of the J-dependence and the method of the reduced matrix elements calculation

In the current paper we concentrate on the excitation of one electron from a closed shell n_0s into an open shell ns or into an empty shell n'''s for the extended model configuration space. The formulae describing the intra- and interconfiguration electrostatically correlated hyperfine interaction are given in the form of the reduced matrix elements using the Wigner-Eckart theorem.

In the case of CHFS for magnetic dipole interactions $K = 1$ the following relations hold:

$$\begin{aligned} &\langle \Psi(\Gamma \alpha S L J M) | \mathbf{CHFS} | \Psi'(\Gamma' \alpha' S' L' J' M') \rangle \\ &= - \sum_{\Psi'' \neq \Psi, \Psi'} \left[\langle \Psi | \mathbf{G} | \Psi'' \rangle \times \langle \Psi'' | \mathbf{t}^{\kappa k} | \Psi' \rangle + \langle \Psi | \mathbf{t}^{\kappa k} | \Psi'' \rangle \times \langle \Psi'' | \mathbf{G} | \Psi' \rangle \right] / \Delta E \\ &= \delta(M, M') \delta(J, J') \sqrt{\frac{3(2J+1)}{J(J+1)}} \begin{Bmatrix} S & S' & \kappa \\ L & L' & k \\ J & J & 1 \end{Bmatrix} \langle \Psi(\Gamma \alpha S L) \| \mathbf{CHFS} \| \Psi'(\Gamma' \alpha' S' L') \rangle \\ &= \delta(M, M') \delta(J, J') \sqrt{\frac{3(2J+1)}{J(J+1)}} \begin{Bmatrix} S & S' & \kappa \\ L & L' & k \\ J & J & 1 \end{Bmatrix} \end{aligned}$$

$$\times \Bigg[-\sum_{\psi''} \left\langle n_0 l_0^{4l_0+2}\ {}^1S, \Gamma\alpha SL; SL\,|\mathbf{G}|\,n_0 l_0^{4l_0+1}\ {}^2l_0, \Gamma''\alpha'' S''L''; SL\right\rangle$$
$$\times \left\langle n_0 l_0^{4l_0+1}\ {}^2l_0, \Gamma''\alpha'' S''L''; SL\,\left\|\mathbf{t}^{\kappa k}\right\|\,n_0 l_0^{4l_0+2}\ {}^1S, \Gamma'\alpha' S'L'; S'L'\right\rangle$$
$$- \sum_{\psi''} \left\langle n_0 l_0^{4l_0+1}\ {}^2l_0, \Gamma''\alpha'' S''L''; SL\,\left\|\mathbf{t}^{\kappa k}\right\|\,n_0 l_0^{4l_0+2}\ {}^1S, \Gamma'\alpha' S'L'; S'L'\right\rangle$$
$$\times \left\langle n_0 l_0^{4l_0+2}\ {}^1S, \Gamma'\alpha' S'L'; S'L'\,|\mathbf{G}|\,n_0 l_0^{4l_0+2}\ {}^1S, \Gamma'\alpha' S'L'\right\rangle \Bigg]$$
$$= \delta(M, M')\ \delta(J, J') \sqrt{\frac{3(2J+1)}{J(J+1)}} \begin{Bmatrix} S & S' & \kappa \\ L & L' & k \\ J & J & 1 \end{Bmatrix} t^{\kappa k}_{coeff}(n_0 l_0, n_i l_i)$$
$$\times (\text{angular part}) \sum_{n_0 l_0} R^t\,(n_i l_i n_0 l_0, n_i l_i n_i' l_i')\,\langle n_0 l_0 | r^{-3} | n_i l_i\rangle / \Delta E, \tag{3}$$

where Γ, Γ' designate configurations being studied, ΔE is the (positive) energy difference between the relevant closed- and open- or empty-shell orbitals, $\kappa k = 10$ and $t^{\kappa k}_{coeff}(n_0 l_0, n_i l_i)$ is the angular part of the hfs operator $\mathbf{t}^{\kappa k}$:

$$\left\langle n_0 l_0 \left\| t^{\kappa k} \right\| n_i l_i \right\rangle = t^{\kappa k}_{coeff}(n_0 l_0, n_i l_i)\ \langle n_0 l_0 | r^{-3} | n_i l_i\rangle^{\kappa k}. \tag{4}$$

The radial integrals of the hfs operator $\mathbf{t}^{\kappa k}$ corresponding to $\kappa k = 10$ is defined as

$$\left\langle n_0 l_0 \left\| t^{10} \right\| n_i l_i \right\rangle = \left\langle n_0 l_0 \left\| \widehat{s}_i r^{-3} \right\| n_i l_i \right\rangle = \delta(l_0, l_i)\sqrt{3/2}\sqrt{2l_0+1}\langle n_0 l_0 | r^{-3} | n_i l_0\rangle^{10}. \tag{5}$$

The formulae (reduced matrix elements) describing the effects of ns core polarization are presented below.

4.3 nl^N configuration

The states ψ and ψ' for the nl^N configuration are defined as follows:

$$\psi = n_0 s^2\ {}^1S, nl^N \alpha SL; \alpha SL,$$
$$\psi' = n_0 s^2\ {}^1S, nl^N \alpha' S'L'; \alpha' S'L'.$$

For the excitation of one electron from a closed n_0s^2 shell into an empty n'''s shell the perturbing virtual states are defined as $\psi'' = n_0 s\ {}^2S, (nl^N \alpha_1'' S_1'' L_1'', n'''s) S''L''; S'''L'''$.

To calculate the matrix elements the formula (29) from the paper [5] should be used.

4.4 $nl^N n_1 l_1^{N_1}$ configuration

The states ψ and ψ' for the $nl^N n_1 l_1^{N_1}$ configuration are defined as follows:

$$\psi = n_0 s^2\ {}^1S, (nl^N \alpha_1 S_1 L_1, n_1 l_1^{N_1} \alpha_2 S_2 L_2) SL; SL,$$
$$\psi' = n_0 s^2\ {}^1S, (nl^N \alpha_1' S_1' L_1', n_1 l_1^{N_1} \alpha_2' S_2' L_2') S'L'; S'L'.$$

If $N_1 = 1$ and $n_1 l_1$-electron is n_1s-electron the excitation from a closed n_0s^2 shell into an open n_1s shell should be considered.

In this case the perturbing virtual states are defined as

$$\psi'' = (n_0 s\ {}^2S, nl^N \alpha_1'' S_1'' L_1'') S''L'', n_1 s^2\ {}^1S; S''L''.$$

To calculate the matrix elements describing this interaction formula (32) from the paper [5] should be used.

In other cases, use the formulas presented in the following subsubsection.

4.4.1 Excitation of one electron from a closed n_0s^2 shell to an empty $n'''s$ shell

In this case the perturbing virtual states are defined as
$\psi'' = (n_0 s\, n'''s)^{2\sigma+1}S, (nl^N\alpha_1''S_1''L_1'', n_1l_1^{N_1}\alpha_2''S_2''L_2'')S''L''; S'''L'''$.

The first type of electrostatic integrals:

$$
\begin{aligned}
&-\sum_{\psi''\neq\psi,\psi'}\left[\langle\psi|\mathbf{G}|\psi''\rangle\times\langle\psi''\|\mathbf{t^{10}}\|\psi'\rangle+\langle\psi\|\mathbf{t^{10}}\|\psi''\rangle\times\langle\psi''|\mathbf{G}|\psi'\rangle\right]/\Delta E\\
&= N\ \delta(\alpha_2S_2L_2,\alpha_2''S_2''L_2'')\ \delta(\alpha_2''S_2''L_2'',\alpha_2'S_2'L_2')\ \delta(\sigma,1)\ \delta(L,L')\ \delta(L_1,L_1')\ \delta(t,l)\ [S_1',S_1,S',S,L]^{1/2}\\
&\times\Bigg[\delta(S''L'',S'L')\ \delta(\alpha_1''S_1''L_1'',\alpha_1'S_1'L_1')\begin{Bmatrix}S_2 & S & S_1\\ 1 & S_1' & S'\end{Bmatrix}\sum_{\bar\alpha\bar S\bar L}\left(nl^N\alpha_1S_1L_1\{|nl^{N-1}\bar\alpha\bar S\bar L\right)\\
&\times\left(nl^N\alpha_1'S_1'L_1'\{|nl^{N-1}\bar\alpha\bar S\bar L\right)(-1)^{3S+2S'+3S_1'+3S_1+S_2+\bar S+1/2}\begin{Bmatrix}1/2 & 1/2 & 1\\ S_1 & S_1' & \bar S\end{Bmatrix}\\
&+\delta(S''L'',SL)\ \delta(\alpha_1''S_1''L_1'',\alpha_1S_1L_1)\begin{Bmatrix}S_2 & S' & S_1'\\ 1 & S_1 & S\end{Bmatrix}\sum_{\bar\alpha'\bar S'\bar L'}\left(nl^N\alpha_1S_1L_1\{|nl^{N-1}\bar\alpha'\bar S'\bar L'\right)\\
&\times\left(nl^N\alpha_1'S_1'L_1'\{|nl^{N-1}\bar\alpha'\bar S'\bar L'\right)(-1)^{S+3S_1'+3S_1+S_2+\bar S+1/2}\begin{Bmatrix}1/2 & 1/2 & 1\\ S_1' & S_1 & \bar S'\end{Bmatrix}\Bigg]\\
&\times\begin{pmatrix}l & l & 0\\ 0 & 0 & 0\end{pmatrix}^2\sum_{n_0s}R^l(n_0s\ nl,nl\ n'''s)\langle n_0s|r^{-3}|n'''s\rangle^{10}/\Delta E.
\end{aligned}
\tag{6}
$$

The second type of electrostatic integrals:

$$
\begin{aligned}
&-\sum_{\psi''\neq\psi,\psi'}\left[\langle\psi|\mathbf{G}|\psi''\rangle\times\langle\psi''\|\mathbf{t^{10}}\|\psi'\rangle+\langle\psi\|\mathbf{t^{10}}\|\psi''\rangle\times\langle\psi''|\mathbf{G}|\psi'\rangle\right]/\Delta E\\
&= N_1\ \delta(\alpha_1S_1L_1,\alpha_1''S_1''L_1'')\ \delta(\alpha_1''S_1''L_1'',\alpha_1'S_1'L_1')\ \delta(\sigma,1)\ \delta(L,L')\ \delta(L_2,L_2')\ \delta(t,l_1)\ [S_2',S_2,S',S,L]^{1/2}\\
&\times\Bigg[\delta(S''L'',S'L')\ \delta(\alpha_2''S_2''L_2'',\alpha_2'S_2'L_2')\begin{Bmatrix}S_1 & S & S_2\\ 1 & S_2' & S'\end{Bmatrix}\sum_{\bar\alpha\bar S\bar L}\left(n_1l_1^{N_1}\alpha_2S_2L_2\{|n_1l_1^{N_1-1}\bar\alpha\bar S\bar L\right)\\
&\times\left(n_1l_1^{N_1}\alpha_2'S_2'L_2'\{|n_1l_1^{N_1-1}\bar\alpha\bar S\bar L\right)(-1)^{3S+2S'+3S_2'+3S_2+S_1+\bar S+1/2}\begin{Bmatrix}1/2 & 1/2 & 1\\ S_2 & S_2' & \bar S\end{Bmatrix}\\
&+\delta(S''L'',SL)\ \delta(\alpha_2''S_2''L_2'',\alpha_2S_2L_2)\begin{Bmatrix}S_1 & S' & S_2'\\ 1 & S_2 & S\end{Bmatrix}\sum_{\bar\alpha'\bar S'\bar L'}\left(n_1l_1^{N_1}\alpha_2S_2L_2\{|n_1l_1^{N_1-1}\bar\alpha'\bar S'\bar L'\right)\\
&\times\left(n_1l_1^{N_1}\alpha_2'S_2'L_2'\{|n_1l_1^{N_1-1}\bar\alpha'\bar S'\bar L'\right)(-1)^{S+3S_2'+3S_2+S_1+\bar S+1/2}\begin{Bmatrix}1/2 & 1/2 & 1\\ S_2' & S_2 & \bar S'\end{Bmatrix}\Bigg]\\
&\times\begin{pmatrix}l_1 & l_1 & 0\\ 0 & 0 & 0\end{pmatrix}^2\sum_{n_0s}R^{l_1}(n_0s\ n_1l_1,n_1l_1\ n'''s)\langle n_0s|r^{-3}|n'''s\rangle^{10}/\Delta E.
\end{aligned}
\tag{7}
$$

4.5 $nl^Nn_1s\ n_2s$ configuration

The states ψ and ψ' for the $nl^Nn_1l_1^{N_1}n_2l_2$ configuration are defined as follows:

$$
\begin{aligned}
\psi &= (n_0s^2\ {}^1S, nl^N\alpha_1S_1L_1)S_1L_1, (n_1sn_2s)S_2L_2; SL,\\
\psi' &= (n_0s^2\ {}^1S, nl^N\alpha_1'S_1'L_1')S_1'L_1', (n_1sn_2s)S_2'L_2'; S'L'.
\end{aligned}
$$

4.5.1 Excitation of one electron from a open n_1s shell into an open n_2s shell

In this case the perturbing virtual states are defined as $\psi'' = n_0 s^2\ {}^1S, nl^N \alpha_1'' S_1'' L_1'', n_2 s^2\ {}^1S; S_1'' L_1''$.

$$
\begin{aligned}
&- \sum_{\psi'' \neq \psi, \psi'} \left[\langle \psi | \mathbf{G} | \psi'' \rangle \times \langle \psi'' \| \mathbf{t^{10}} \| \psi' \rangle + \langle \psi \| \mathbf{t^{10}} \| \psi'' \rangle \times \langle \psi'' | \mathbf{G} | \psi' \rangle \right] / \Delta E \\
&= \frac{\sqrt{2}\ N}{\sqrt{3}\sqrt{2l+1}}\ \delta(t,0) \Bigg[\delta(SL, S_1 L_1)\ \delta(S_1'' L_1'', SL)\ \delta(\alpha_1' S_1' L_1', \alpha SL)\ \delta(S_2, 0)\ \delta(L_2, 0)\ \delta(S_2', 1)\ \delta(L_2', 0) \\
&\times (-1)^{3S+S'+L+L'}\ [S', L']^{1/2} \sum_{\bar{\alpha} \bar{S} \bar{L}} \left(nl^N \alpha S L \{ | nl^{N-1} \bar{\alpha} \bar{S} \bar{L} \right) \left(nl^N \alpha_1'' S_1'' L_1'' \{ | nl^{N-1} \bar{\alpha} \bar{S} \bar{L} \right) \\
&+ \delta(S'L', S_1'' L_1'')\ \delta(S'L', S_1' L_1')\ \delta(\alpha_1 S_1 L_1, \alpha' S' L')\ \delta(S_2', 0)\ \delta(L_2', 0)\ \delta(S_2, 1)\ \delta(L_2, 0)\ (-1)^{2S+2S'} \\
&\times [S, L]^{1/2} \sum_{\bar{\alpha}' \bar{S}' \bar{L}'} \left(nl^N \alpha' S' L' \{ | nl^{N-1} \bar{\alpha}' \bar{S}' \bar{L}' \right) \left(nl^N \alpha_1'' S_1'' L_1'' \{ | nl^{N-1} \bar{\alpha}' \bar{S}' \bar{L}' \right) \Bigg] \\
&\times (l \| \mathbf{C}^0 \| l)(0 \| \mathbf{C}^0 \| 0) R^0 (nln_1 s, nln_2 s) \langle n_1 s | r^{-3} | n_2 s \rangle^{10} / \Delta E \\
&+ \frac{N}{\sqrt{3}(2l+1)}\ \delta(l,t) \Bigg[\delta(S_1'' L_1'', SL)\ \delta(\alpha_1' S_1' L_1', \alpha SL)\ \delta(L_2, 0)\ \delta(L_1, L)\ \delta(S_2', 1)\ \delta(L_2', 0)\ [S', L', S_1, S_2]^{1/2} \\
&\times \sum_{\bar{\alpha} \bar{S} \bar{L}} \left(nl^N \alpha S L \{ | nl^{N-1} \bar{\alpha} \bar{S} \bar{L} \right) \left(nl^N \alpha_1'' S_1'' L_1'' \{ | nl^{N-1} \bar{\alpha} \bar{S} \bar{L} \right) (-1)^{3\bar{S}+2S+S'+3S_2+L+L'+l+1/2} \begin{Bmatrix} \bar{S} & 1/2 & S_1 \\ S_2 & S & 1/2 \end{Bmatrix} \\
&+ \delta(S_1'' L_1'', S'L')\ \delta(\alpha_1 S_1 L_1, \alpha' S' L')\ \delta(L_2', 0)\ \delta(L_1', L')\ \delta(S_2, 1)\ \delta(L_2, 0)\ [S, L, S_1', S_2']^{1/2} \\
&\times \sum_{\bar{\alpha}' \bar{S}' \bar{L}'} \left(nl^N \alpha' S' L' \{ | nl^{N-1} \bar{\alpha}' \bar{S}' \bar{L}' \right) \left(nl^N \alpha_1'' S_1'' L_1'' \{ | nl^{N-1} \bar{\alpha}' \bar{S}' \bar{L}' \right) (-1)^{3\bar{S}'+2S+S'+3S_2'+l+1/2} \begin{Bmatrix} \bar{S}' & 1/2 & S_1' \\ S_2' & S' & 1/2 \end{Bmatrix} \Bigg] \\
&\times (l \| \mathbf{C}^l \| 0)(0 \| \mathbf{C}^l \| l) R^l (nln_1 s, n_2 snl) \langle n_1 s | r^{-3} | n_2 s \rangle^{10} / \Delta E. \qquad (8)
\end{aligned}
$$

4.6 $nl^N n_1 l_1^{N_1} n_2 l_2$ configuration

The states ψ and ψ' for the $nl^N n_1 l_1^{N_1} n_2 l_2$ configuration are defined as follows:

$$
\begin{aligned}
\psi &= (n_0 s^2\ {}^1S, nl^N \alpha_1 S_1 L_1) S_1 L_1, (n_1 l_1^{N_1} \alpha_2 S_2 L_2, n_2 l_2) S_3 L_3; SL, \\
\psi' &= (n_0 s^2\ {}^1S, nl^N \alpha_1' S_1' L_1') S_1' L_1', (n_1 l_1^{N_1} \alpha_2' S_2' L_2', n_2 l_2) S_3' L_3'; S'L'.
\end{aligned}
$$

If $N_1 = 1$ and $n_1 l_1$-electron is n_1s-electron the excitation from a closed n_0s^2 shell into an open n_1s shell should be considered.

In this case the perturbing virtual states are defined as

$$
\psi'' = (n_0 s\ {}^2S, nl^N \alpha_1'' S_1'' L_1'') S'' L'', (n_1 s^2\ {}^1S, n_2 l_2) S_3'' L_3''; S''' L'''.
$$

To calculate the matrix elements describing this interaction formulae (37), (38) and (39) from the paper [5] should be used.

If $n_2 l_2$-electron is n_2s-electron the excitation from a closed n_0s^2 shell into an open n_2s shell should be considered.

In this case the perturbing virtual states are defined as

$$
\psi'' = (n_0 s\ {}^2S, nl^N \alpha_1'' S_1'' L_1'') S'' L'', (n_1 l_1^{N_1} \alpha_2'' S_2'' L_2'', n_2 s^2\ {}^1S) S_3'' L_3''; S''' L'''.
$$

To calculate the matrix elements describing this interaction formulae (40), (41) and (42) from the paper [5] should be used.

In other cases, use the formulas presented in the following paragraph.

4.6.1 Excitation of one electron from a closed n_0s^2 shell to an empty $n'''s$ shell

In this case the perturbing virtual states are defined as
$\psi'' = ((n_0 s\ n'''s)^{2\sigma+1}S, nl^N\alpha_1''S_1''L_1'')S''L'', (n_1 l_1^{N_1}\alpha_2''S_2''L_2'', n_2 l_2)\ S_3''L_3''; S'''L'''$.

The first type of electrostatic integrals:

$$
\begin{aligned}
&-\sum_{\psi''\neq\psi,\psi'}\left[\langle\psi|\mathbf{G}|\psi''\rangle\times\langle\psi''\|\mathbf{t^{10}}\|\psi'\rangle+\langle\psi\|\mathbf{t^{10}}\|\psi''\rangle\times\langle\psi''|\mathbf{G}|\psi'\rangle\right]/\Delta E\\
&=N\ \delta(\alpha_2S_2L_2,\alpha_2''S_2''L_2'')\ \delta(\alpha_2''S_2''L_2'',\alpha_2'S_2'L_2')\ \delta(S_3L_3,S_3''L_3'')\ \delta(S_3''L_3'',S_3'L_3')\ \delta(\sigma,1)\ \delta(L,L')\ \delta(L_1,L_1')\ \delta(t,l)\\
&\times[S,L,S']^{1/2}\Bigg[\delta(S''L'',S_1L_1)\ \delta(L_1,L_1'')\ \delta(\alpha_1''S_1''L_1'',\alpha_1'S_1'L_1')\ [S_1'',S''']^{1/2}\begin{Bmatrix}S & S' & 1\\ S_1' & S'' & S_3'\end{Bmatrix}\\
&\times\sum_{\bar\alpha\bar S\bar L}\left(nl^N\alpha_1S_1L_1\{|nl^{N-1}\bar\alpha\bar S\bar L\right)\left(nl^N\alpha_1'S_1'L_1'\{|nl^{N-1}\bar\alpha\bar S\bar L\right)(-1)^{S'+2S_1'+S_3'+2S''+3\bar S+3/2}\begin{Bmatrix}1/2 & 1/2 & 1\\ S_1'' & S_1 & \bar S\end{Bmatrix}\\
&+\delta(S''L'',S_1'L_1')\ \delta(\alpha_1''S_1''L_1'',\alpha_1S_1L_1)\ \delta(L_1',L_1'')\ [S_1'',S''']^{1/2}\begin{Bmatrix}S & S' & 1\\ S'' & S_1 & S_3\end{Bmatrix}\sum_{\bar\alpha'\bar S'\bar L'}\left(nl^N\alpha_1S_1L_1\{|nl^{N-1}\bar\alpha'\bar S'\bar L'\right)\\
&\times\left(nl^N\alpha_1'S_1'L_1'\{|nl^{N-1}\bar\alpha'\bar S'\bar L'\right)(-1)^{S'+2S_1+2S''+S_3+3\bar S+3/2}\begin{Bmatrix}1/2 & 1/2 & 1\\ S_1'' & S_1' & \bar S'\end{Bmatrix}\Bigg]\\
&\times\begin{pmatrix}l & l & 0\\ 0 & 0 & 0\end{pmatrix}^2\sum_{n_0s}R^l(n_0s\ nl,nl\ n'''s)\langle n_0s|r^{-3}|n'''s\rangle^{10}/\Delta E.
\end{aligned}
\tag{9}
$$

The second type of electrostatic integrals:

$$
\begin{aligned}
&-\sum_{\psi''\neq\psi,\psi'}\left[\langle\psi|\mathbf{G}|\psi''\rangle\times\langle\psi''\|\mathbf{t^{10}}\|\psi'\rangle+\langle\psi\|\mathbf{t^{10}}\|\psi''\rangle\times\langle\psi''|\mathbf{G}|\psi'\rangle\right]/\Delta E\\
&=N_1\ \delta(\alpha_1S_1L_1,\alpha_1''S_1''L_1'')\ \delta(\alpha_1''S_1''L_1'',\alpha_1'S_1'L_1')\ \delta(\sigma,1)\ \delta(L,L')\ \delta(L_2,L_2')\ \delta(L_3,L_3')\ \delta(t,l_1)\ [S_2,S_2',S_3,S_3',S',S,L]^{1/2}\\
&\times\Bigg[\delta(S_3''L_3'',S_3'L_3')\ \delta(\alpha_2''S_2''L_2'',\alpha_2'S_2'L_2')\ \delta(L'',L_1')\ [S'']\begin{Bmatrix}S & S' & 1\\ S_1' & S'' & S_3'\end{Bmatrix}\begin{Bmatrix}S_2' & S_2 & 1\\ S_3 & S_3' & 1/2\end{Bmatrix}\begin{Bmatrix}S'' & S_3' & S\\ S_3 & S_1 & 1\end{Bmatrix}\\
&\times\sum_{\bar\alpha\bar S\bar L}\left(n_1l_1^{N_1}\alpha_2S_2L_2\{|n_1l_1^{N_1-1}\bar\alpha\bar S\bar L\right)\left(n_1l_1^{N_1}\alpha_2'S_2'L_2'\{|n_1l_1^{N_1-1}\bar\alpha\bar S\bar L\right)(-1)^{S+S'+3S_3+2S_3'+2S_2+3S_1'+3S''+3\bar S}\begin{Bmatrix}1/2 & 1/2 & 1\\ S_2 & S_2' & \bar S\end{Bmatrix}\\
&+\delta(S_3''L_3'',S_3L_3)\ \delta(\alpha_2''S_2''L_2'',\alpha_2S_2L_2)\ \delta(L'',L_1)\ [S'']\begin{Bmatrix}S & S' & 1\\ S'' & S_1 & S_3\end{Bmatrix}\begin{Bmatrix}S_2' & S_2 & 1\\ S_3 & S_3' & 1/2\end{Bmatrix}\begin{Bmatrix}S'' & S_3 & S'\\ S_3' & S_1' & 1\end{Bmatrix}\\
&\times\sum_{\bar\alpha'\bar S'\bar L'}\left(n_1l_1^{N_1}\alpha_2S_2L_2\{|n_1l_1^{N_1-1}\bar\alpha'\bar S'\bar L'\right)\left(n_1l_1^{N_1}\alpha_2'S_2'L_2'\{|n_1l_1^{N_1-1}\bar\alpha'\bar S'\bar L'\right)(-1)^{2S'+2S_2'+2S_3+3S_3'+3S_1+3S''+3\bar S}\\
&\times\begin{Bmatrix}1/2 & 1/2 & 1\\ S_2' & S_2 & \bar S'\end{Bmatrix}\Bigg]\begin{pmatrix}l_1 & l_1 & 0\\ 0 & 0 & 0\end{pmatrix}^2\sum_{n_0s}R^{l_1}(n_0s\ n_1l_1,n_1l_1\ n'''s)\langle n_0s|r^{-3}|n'''s\rangle^{10}/\Delta E.
\end{aligned}
\tag{10}
$$

The third type of electrostatic integrals:

$$
\begin{aligned}
&-\sum_{\psi''\neq\psi,\psi'}\left[\langle\psi|\mathbf{G}|\psi''\rangle\times\langle\psi''\|\mathbf{t^{10}}\|\psi'\rangle+\langle\psi\|\mathbf{t^{10}}\|\psi''\rangle\times\langle\psi''|\mathbf{G}|\psi'\rangle\right]/\Delta E\\
&=\delta(\alpha_1S_1L_1,\alpha_1''S_1''L_1'')\ \delta(\alpha_1''S_1''L_1'',\alpha_1'S_1'L_1')\ \delta(\alpha_2S_2L_2,\alpha_2''S_2''L_2'')\ \delta(\alpha_2''S_2''L_2'',\alpha_2'S_2'L_2')\ \delta(L_3,L_3')\ \delta(L'',L_1')\\
&\times\delta(\sigma,1)\ \delta(L,L')\ \delta(t,l_2)\ [S_3,S_3',S,L,S']^{1/2}\\
&\times\Bigg[\delta(S_3''L_3'',S_3'L_3')\ \delta(L_1',L'')\ [S'']\begin{Bmatrix}S'' & S_3' & S\\ S_3 & S_1 & 1\end{Bmatrix}\begin{Bmatrix}S & S' & 1\\ S_1' & S'' & S_3'\end{Bmatrix}\begin{Bmatrix}1/2 & 1/2 & 1\\ S_3 & S_3' & S_2\end{Bmatrix}(-1)^{S_2+S+S'+3S_1'+2S_3+S_3'+3S''+1/2}\\
&+\delta(S_3''L_3'',S_3L_3)\ \delta(L_1,L'')\ [S'']\begin{Bmatrix}S'' & S_3 & S'\\ S_3' & S_1' & 1\end{Bmatrix}\begin{Bmatrix}S & S' & 1\\ S'' & S_1 & S_3\end{Bmatrix}\begin{Bmatrix}1/2 & 1/2 & 1\\ S_3 & S_3' & S_2'\end{Bmatrix}(-1)^{S_2'+2S'+3S_1+S_3+2S_3'+3S''+1/2}\Bigg]\\
&\times\begin{pmatrix}l_2 & l_2 & 0\\ 0 & 0 & 0\end{pmatrix}^2\sum_{n_0s}R^{l_2}(n_0s\ n_2l_2,n_2l_2\ n'''s)\langle n_0s|r^{-3}|n'''s\rangle^{10}/\Delta E.
\end{aligned}
\tag{11}
$$

4.7 Interconfiguration interaction

4.7.1 Configuration interaction $nl^N n_1 l_1 \leftrightarrow nl^{N-1} n_2 s\ n_1 l_1$

The states ψ for the $nl^N n_1 l_1$ configuration and ψ' for the $nl^{N-1} n_2 s\ n_1 l_1$ configuration are defined as follows:

$$\psi = (n_0 s^2\ {}^1S, nl^N \alpha_1 S_1 L_1)\alpha_1 S_1 L_1, n_1 l_1; SL,$$
$$\psi' = (n_0 s^2\ {}^1S, nl^{N-1} \alpha'_1 S'_1 L'_1)\alpha'_1 S'_1 L'_1, (n_2 s\ n_1 l_1) S'_3 L'_3; S' L'.$$

For the excitation of an electron from a closed n_0s^2 shell into an empty n_2s shell the perturbing virtual states are defined as $\psi'' = (n_0 s\ {}^2S, nl^N\ \alpha''_1 S''_1 L''_1) S'' L'', (n_1 l_1\ n_2 s) S''_3 L''_3; S''' L'''$.

In this case the first term of the sum below is equal to zero due to hyperfine interaction:

$$-\sum_{\psi'' \neq \psi, \psi'} \left[\langle \psi | \mathbf{G} | \psi'' \rangle \times \langle \psi'' \| \mathbf{t^{10}} \| \psi' \rangle + \langle \psi \| \mathbf{t^{10}} \| \psi'' \rangle \times \langle \psi'' | \mathbf{G} | \psi' \rangle \right] / \Delta E. \tag{12}$$

The second component is as follows:

$$\begin{aligned}
&-\sum_{\psi''} \langle \psi \| \mathbf{t^{10}} \| \psi'' \rangle \times \langle \psi'' | \mathbf{G} | \psi' \rangle / \ \Delta E \\
&= -\sum_{\psi''} \sqrt{N}\ \delta(\alpha_1 S_1 L_1, \alpha''_1 S''_1 L''_1)\ \delta(L, L')\ \delta(L_1, L'')\ \delta(S'_3 L'_3, S''_3 L''_3)\ \delta(S'_1 L'_1, S'' L'')\ \delta(L'_1, L''_1)\ \delta(l, t) \\
&\times \frac{[S, L, S', S_1, S'_3]^{1/2}}{[L'_1]^{1/2}} (-1)^{3S'_1+3S_1+S+S'+3S'_3+L'_3+L'_1+l_1+0.5} \begin{Bmatrix} 1/2 & 1/2 & 1 \\ 1/2 & S_1 & S \\ S'_3 & S'_1 & S' \end{Bmatrix} \sum_{\bar{\alpha}\bar{S}\bar{L}} \delta(\bar{S}, S'_1) \left(nl^N \alpha_1 S_1 L_1 \{ | nl^{N-1} \bar{\alpha} \bar{S} \bar{L} \right) \\
&\times \left\langle nl^{N-1} \bar{\alpha} \bar{S} \bar{L} \left\| \mathbf{U}^l \right\| nl^{N-1} \alpha'_1 S'_1 L'_1 \right\rangle\ (-1)^{\bar{L}} (2l+1) \begin{pmatrix} l & l & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l & 0 \\ 0 & 0 & 0 \end{pmatrix} \sum_{n_0 s}\ R^l(n_0 s\ nl, nlnl) \langle n_0 s | r^{-3} | n_2 s \rangle^{10} / \Delta E.
\end{aligned} \tag{13}$$

4.7.2 Configuration interaction $nl^N n_2 s\ n_1 l_1 \leftrightarrow nl^{N-1} n_2 s^2 n_1 l_1$

The states ψ for the $nl^N n_2 s\ n_1 l_1$ configuration and ψ' for the $nl^{N-1}\ n_2 s^2 n_1 l_1$ configuration are defined as follows:

$$\psi = (n_0 s^2\ {}^1S, nl^N \alpha_1 S_1 L_1)\alpha_1 S_1 L_1, (n_2 s\ n_1 l_1) S_3 L_3; SL,$$
$$\psi' = (n_0 s^2\ {}^1S, nl^{N-1} \alpha'_1 S'_1 L'_1)\alpha'_1 S'_1 L'_1, (n_2 s^2\ {}^1S, n_1 l_1) S'_3 L'_3; S' L'.$$

For the excitation of an electron from a closed n_0s^2 shell into an open n_2s shell the perturbing virtual states are defined as $\psi'' = (n_0 s\ {}^2S, nl^N\ \alpha''_1 S''_1 L''_1) S'' L'', (n_2 s^2\ {}^1S, n_1 l_1) S''_3 L''_3; S''' L'''$.

In this case the first term of the sum below is equal to zero due to hyperfine interaction:

$$-\sum_{\psi'' \neq \psi, \psi'} \left[\langle \psi | \mathbf{G} | \psi'' \rangle \times \langle \psi'' \| \mathbf{t^{10}} \| \psi' \rangle + \langle \psi \| \mathbf{t^{10}} \| \psi'' \rangle \times \langle \psi'' | \mathbf{G} | \psi' \rangle \right] / \Delta E. \tag{14}$$

The second component is as follows:

$$\begin{aligned}
&-\sum_{\psi''} \langle \psi \| \mathbf{t^{10}} \| \psi'' \rangle \times \langle \psi'' | \mathbf{G} | \psi' \rangle / \ \Delta E \\
&= -\sum_{\psi''} \sqrt{N}\ \delta(\alpha_1 S_1 L_1, \alpha''_1 S''_1 L''_1)\ \delta(L, L')\ \delta(L_1, L'')\ \delta(L_3, l_1) \delta(S'_3 L'_3, S''_3 L''_3)\ \delta(S'_1 L'_1, S'' L'')\ \delta(L'_1, L''_1)\ \delta(l, t) \\
&\times \frac{[S, L, S', S_1, S_3]^{1/2}}{[L'_1]^{1/2}} (-1)^{2S'_1+S_3+2S'+L'_1+1} \begin{Bmatrix} 1/2 & 1/2 & 1 \\ 1/2 & S'_1 & S' \\ S_3 & S_1 & S \end{Bmatrix} \sum_{\bar{\alpha}\bar{S}\bar{L}} \delta(\bar{S}, S'_1) \left(nl^N \alpha_1 S_1 L_1 \{ | nl^{N-1} \bar{\alpha} \bar{S} \bar{L} \right) \\
&\times \left\langle nl^{N-1} \bar{\alpha} \bar{S} \bar{L} \left\| \mathbf{U}^l \right\| nl^{N-1} \alpha'_1 S'_1 L'_1 \right\rangle (-1)^{\bar{L}} (2l+1) \begin{pmatrix} l & l & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l & 0 \\ 0 & 0 & 0 \end{pmatrix} \sum_{n_0 s}\ R^l(n_0 s\ nl, nlnl) \langle n_0 s | r^{-3} | n_2 s \rangle^{10} / \Delta E.
\end{aligned} \tag{15}$$

4.7.3 Configuration interaction $nl^N n_1 l_1^2 \leftrightarrow nl^{N-1} n_2 s\ n_1 l_1^2$

The states ψ for the $nl^N n_1 l_1^2$ configuration and ψ' for the $nl^{N-1} n_2 s\ n_1 l_1^2$ configuration are defined as follows:

$$\psi = (n_0 s^2\ {}^1S, nl^N \alpha_1 S_1 L_1) \alpha_1 S_1 L_1, n_1 l_1^2 \alpha_2 S_2 L_2; SL,$$
$$\psi' = (n_0 s^2\ {}^1S, (nl^{N-1} \alpha_1' S_1' L_1',\ n_2 s)\ S_2' L_2')\ S_2' L_2', n_1 l_1^2 \alpha_3' S_3' L_3'; S' L'.$$

For the excitation of an electron from a closed $n_0 s^2$ shell into an empty $n_2 s$ shell the perturbing virtual states are defined as $\psi'' = (n_0 s\ {}^2S, nl^N \alpha_1'' S_1'' L_1'') S'' L'', (n_1 l_1^2\ \alpha_2'' S_2'' L_2'', n_2 s)\ S_3'' L_3''; S''' L'''$.

In this case the first term of the sum below is equal to zero due to hyperfine interaction:

$$-\sum_{\psi'' \neq \psi, \psi'} \left[\langle \psi | \mathbf{G} | \psi'' \rangle \times \langle \psi'' \| \mathbf{t^{10}} \| \psi' \rangle + \langle \psi \| \mathbf{t^{10}} \| \psi'' \rangle \times \langle \psi'' | \mathbf{G} | \psi' \rangle \right] / \Delta E. \tag{16}$$

The second component is as follows:

$$\begin{aligned}
&-\sum_{\psi''} \langle \psi \| \mathbf{t^{10}} \| \psi'' \rangle \times \langle \psi'' | \mathbf{G} | \psi' \rangle / \ \Delta E \\
&= -\sum_{\psi''} \sqrt{N}\ \delta(\alpha_1 S_1 L_1, \alpha_1'' S_1'' L_1'')\ \delta(\alpha_2 S_2 L_2, \alpha_2'' S_2'' L_2'')\ \delta(L, L')\ \delta(L_1, L'')\ \delta(L_2'', L_3'') \\
&\times\ [S, L, S', S'', S_3'']^{1/2}\ (-1)^{3S''+3S_1+S+S'+1.5} \begin{Bmatrix} 1/2 & 1/2 & 1 \\ S_2 & S_1 & S \\ S_3'' & S'' & S' \end{Bmatrix} \\
&\times \left[\delta(\alpha_3' S_3' L_3', \alpha_2'' S_2'' L_2'')\ \delta(L_1', L_1'')\ \delta(S_1' L_1', S'' L'')\ \delta(L_2', L'')\ \delta(L_2'', L_3'')\ \delta(l, t)\ \frac{[S_2', S_3'', S_1'']^{1/2}}{[S_1', L_1']^{1/2}} \begin{Bmatrix} S_2'' & S' & S_2' \\ S'' & 1/2 & S_3'' \end{Bmatrix} \right. \\
&\times (-1)^{S''+S'+3S_3''+L_3''+L_1''+L_2''} \sum_{\bar{\alpha} \bar{S} \bar{L}} \delta(\bar{S}, S_1') (-1)^{\bar{L}} \left(nl^N \alpha_1'' S_1'' L_1'' \{ | nl^{N-1} \bar{\alpha} \bar{S} \bar{L} \right) \left\langle nl^{N-1} \bar{\alpha} \bar{S} \bar{L} \left\| \mathbf{U}^l \right\| nl^{N-1} \alpha_1' S_1' L_1' \right\rangle \\
&\times\ (2l+1) \begin{pmatrix} l & l & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l & 0 \\ 0 & 0 & 0 \end{pmatrix} \sum_{n_0 s}\ R^l(n_0 s\ nl, nlnl) \langle n_0 s | r^{-3} | n_2 s \rangle^{10} / \Delta E \\
&+ 2\ \delta(S_1', S'')\ \delta(S_3', S_2'')\ \delta(L_1'', L'')\ \delta(L_1', L_2')\ \delta(L_2'', L_3'')\ \delta(t, l) \left(nl^N \alpha_1'' S_1'' L_1'' \{ | nl^{N-1} \alpha_1' S_1' L_1' \right) \\
&\times \frac{[S_2', S_3'', S_1'', L_1'', L_2'', S_3']^{1/2}}{[S_1']^{1/2}} (-1)^{3S'+L'+S''+2S_2'+2S_1''+3S_3''+L+L_1'+l_1+1} \begin{Bmatrix} S_2'' & S' & S_2' \\ S'' & 1/2 & S_3'' \end{Bmatrix} \begin{Bmatrix} L' & L'' & L_2'' \\ t & L_3' & L_2' \end{Bmatrix} \begin{Bmatrix} t & l_1 & l_1 \\ l_1 & L_2'' & L_3' \end{Bmatrix} \\
&\times (2l_1+1) \begin{pmatrix} l & l & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l & l_1 \\ 0 & 0 & 0 \end{pmatrix} \sum_{n_0 s}\ R^l(n_0 s\ n_1 l_1, nln_1 l_1) \langle n_0 s | r^{-3} | n_2 s \rangle^{10} / \Delta E \\
&+ 2\ \delta(L_1', L'')\ \delta(L_1', L_2')\ \delta(L_2'', L_3'')\ \delta(t, l_1) \left(nl^N \alpha_1'' S_1'' L_1'' \{ | nl^{N-1} \alpha_1' S_1' L_1' \right) [S_3'', S'', S_2', S_3', L_3', S_2'', L_2'', S_1'', L_1'']^{1/2} \\
&\times (-1)^{3S_1''+2S'+L'+3S_3''+S''+2S_2'+S_3'+S_2''+L_2'+1} \begin{Bmatrix} S_2' & S_1' & 1/2 & S_2'' \\ S_3' & 1/2 & 1/2 & S'' \\ S' & S_1'' & S_3'' & 1/2 \end{Bmatrix} \begin{Bmatrix} l & L_2' & L'' \\ L' & L_2'' & L_3' \end{Bmatrix} \begin{Bmatrix} l_1 & l_1 & l \\ L_2'' & L_3' & l_1 \end{Bmatrix} \\
&\times \sqrt{2l_1+1}\ \sqrt{2l+1}\ \begin{pmatrix} l_1 & l_1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l & l_1 \\ 0 & 0 & 0 \end{pmatrix} \sum_{n_0 s}\ R^{l_1}(n_0 s\ n_1 l_1, n_1 l_1 nl) \langle n_0 s | r^{-3} | n_2 s \rangle^{10} / \Delta E \Bigg].
\end{aligned} \tag{17}$$

4.7.4 Configuration interaction $nl^N n_1 l_1 \leftrightarrow nl^{N-1} n_3 s\ n_2 l_2$

The states ψ for the $nl^N n_1 l_1$ configuration and ψ' for the $nl^{N-1} n_3 s\ n_2 l_2$ configuration are defined as follows:

$$\psi = (n_0 s^2\ {}^1S, nl^N \alpha_1 S_1 L_1) \alpha_1 S_1 L_1, n_1 l_1; SL,$$
$$\psi' = (n_0 s^2\ {}^1S, nl^{N-1} \alpha_1' S_1' L_1') \alpha_1' S_1' L_1', (n_3 s, n_2 l_2) S_2' L_2'; S' L'.$$

For the excitation of an electron from a closed n_0s^2 shell into an empty n_3s shell the perturbing virtual states are defined as $\psi'' = (n_0 s\ ^2S, nl^N\alpha_1'' S_1'' L_1'')S''L'', (n_1 l_1, n_3 s)S_2'' L_2''; S'''L'''$.

In this case the first term of the sum below is equal to zero due to hyperfine interaction:

$$-\sum_{\psi''\neq\psi,\psi'} \left[\langle\psi|\mathbf{G}|\psi''\rangle \times \langle\psi''\|\mathbf{t^{10}}\|\psi'\rangle + \langle\psi\|\mathbf{t^{10}}\|\psi''\rangle \times \langle\psi''|\mathbf{G}|\psi'\rangle\right]/\Delta E. \tag{18}$$

The second component is as follows:

$$\begin{aligned}
&-\sum_{\psi''} \langle\psi\|\mathbf{t^{10}}\|\psi''\rangle \times \langle\psi''|\mathbf{G}|\psi'\rangle / \Delta E \\
&= -\sum_{\psi''} \sqrt{N}\ \delta(\alpha_1 S_1 L_1, \alpha_1'' S_1'' L_1'')\ \delta(L, L')\ \delta(L_1, L'')\ [S, L, S', S'', S_2'']^{1/2} (-1)^{S''+S'+L'+l+0.5} \begin{Bmatrix} S' & S & 1 \\ S'' & S_1 & 1/2 \\ S_2'' & 1/2 & 1/2 \end{Bmatrix} \\
&\times \left[\delta(S_1', S'')\ \delta(L'', L_1'')\ \delta(S_2', S_2'')\delta(L_2', l_2)\ \delta(L_2'', l_1) \left(nl^N\alpha_1'' S_1'' L_1''\{|nl^{N-1}\alpha_1' S_1' L_1'\right) \frac{[S_1'', L_1'']^{1/2}}{[S_1']^{1/2}} \begin{Bmatrix} l_2 & L' & L_1' \\ L'' & l & l_1 \end{Bmatrix}\right. \\
&\times (-1)^{2S_1'+L_1'+S_2'}\ \delta(l,t)\ \sqrt{(2l_1+1)(2l_2+1)} \begin{pmatrix} l & l & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l & l_2 \\ 0 & 0 & 0 \end{pmatrix} \sum_{n_0 s}\ R^l(n_0 s\ n_2 l_2, nln_1 l_1)\langle n_0 s|r^{-3}|n_2 s\rangle^{10}/\Delta E \\
&+ \delta(L'', L_1'')\ \delta(L_2', l_2)\ \delta(L_2'', l_1)\ [S_2', S_1'', S_2'', S'', L'']^{1/2}\ \left(nl^N\alpha_1'' S_1'' L_1''\{|nl^{N-1}\alpha_1' S_1' L_1'\right) \\
&\times\ (-1)^{2S_1''+S''+S_1'+L_1'+S_2'+l_2+1} \begin{Bmatrix} 1/2 & S_2'' & 1/2 \\ S'' & S_1'' & S' \end{Bmatrix} \begin{Bmatrix} S_2' & S' & S_1' \\ S_1'' & 1/2 & 1/2 \end{Bmatrix} \begin{Bmatrix} l_2 & L' & L_1' \\ L'' & l & l_1 \end{Bmatrix} \\
&\times\ \left.\delta(l_1,t)\ \sqrt{(2l+1)(2l_2+1)} \begin{pmatrix} l_1 & l_1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l_1 & l_2 \\ 0 & 0 & 0 \end{pmatrix} \sum_{n_0 s}\ R^l(n_0 s\ n_2 l_2, n_1 l_1 nl)\langle n_0 s|r^{-3}|n_2 s\rangle^{10}/\Delta E\right].
\end{aligned} \tag{19}$$

4.7.5 Configuration interaction $nl^N n_1 l_1 \leftrightarrow nl^N n_2 s$

The states ψ for the $nl^N n_1 l_1$ configuration and ψ' for the $nl^N n_2 s$ configuration are defined as follows:

$$\psi = (n_0 s^2\ ^1S, nl^N\alpha_1 S_1 L_1)\alpha_1 S_1 L_1, n_1 l_1; SL,$$

$$\psi' = (n_0 s^2\ ^1S, nl^N\alpha_1' S_1' L_1')\alpha_1' S_1' L_1', n_2 s; S'L'.$$

For the excitation of an electron from a closed n_0s^2 shell into an empty n_2s shell the perturbing virtual states are defined as $\psi'' = (n_0 s\ ^2S, nl^N\alpha_1'' S_1'' L_1'')S''L'', (n_1 l_1, n_2 s)S_2'' L_2''; S'''L'''$.

In this case the first term of the sum below is equal to zero due to hyperfine interaction (hfs operator is acting between electrons n_0s and $n_1 l_1$, radial integral $\langle n_0 s|r^{-3}|n_1 l_1\rangle^{10} \approx 0$):

$$-\sum_{\psi''\neq\psi,\psi'} \left[\langle\psi|\mathbf{G}|\psi''\rangle \times \langle\psi''\|\mathbf{t^{10}}\|\psi'\rangle + \langle\psi\|\mathbf{t^{10}}\|\psi''\rangle \times \langle\psi''|\mathbf{G}|\psi'\rangle\right]/\Delta E. \tag{20}$$

The second component is as follows:

$$\begin{aligned}
&-\sum_{\psi''} \langle\psi\|\mathbf{t^{10}}\|\psi''\rangle \times \langle\psi''|\mathbf{G}|\psi'\rangle / \Delta E \\
&= -\sum_{\psi''} \delta(\alpha_1 S_1 L_1, \alpha_1'' S_1'' L_1'')\ \delta(L, L')\ \delta(L_1, L'')\ [S, L, S', S'', S_2'']^{1/2}\ (-1)^{3S''+3S_1+S+S'+1.5} \begin{Bmatrix} 1/2 & 1/2 & 1 \\ 1/2 & S_1 & S \\ S_2'' & S'' & S' \end{Bmatrix} \\
&\times \left[\sum_{\bar\alpha\bar S\bar L} N\ \delta(L'', L_1'')\ \delta(\bar S, S'')\ \left(nl^N\alpha_1'' S_1'' L_1''\{|nl^{N-1}\bar\alpha\bar S\bar L\right)\ \left(nl^N\alpha_1' S_1' L_1'\{|nl^{N-1}\bar\alpha\bar S\bar L\right)\right. \\
&\times (-1)^{2S_1'+3S''+S'+\bar L+L_1'+l+1}\ \frac{[S_1', S_1'', S_2'', L'']^{1/2}}{[S'']^{1/2}} \begin{Bmatrix} \bar L & l & L'' \\ l_1 & L_1' & l \end{Bmatrix} \begin{Bmatrix} 1/2 & S' & S_1' \\ S'' & 1/2 & S_2'' \end{Bmatrix}
\end{aligned}$$

$$\times \delta(l,t)\ \sqrt{(2l+1)(2l_1+1)} \begin{pmatrix} l & l & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l & l \\ 0 & 0 & 0 \end{pmatrix} \sum_{n_0 s}\ R^l(n_0 s\ nl, nln_1l_1)\langle n_0 s|r^{-3}|n_2 s\rangle^{10}/\Delta E$$

$$+ \sum_{\bar{\alpha}\bar{S}\bar{L}} N\ \delta(L'', L_1'')\ \delta(S_1', S_1'')\ \left(nl^N \alpha_1'' S_1'' L_1'' \{|nl^{N-1}\bar{\alpha}\bar{S}\bar{L}\right)\ \left(nl^N \alpha_1' S_1' L_1' \{|nl^{N-1}\bar{\alpha}\bar{S}\bar{L}\right)$$

$$\times (-1)^{2S_1'+3S''+S'+\bar{L}+L_1'}\ [S_2'', S'', L'']^{1/2} \begin{Bmatrix} \bar{L} & l & L'' \\ l_1 & L_1' & l \end{Bmatrix} \begin{Bmatrix} 1/2 & S' & S_1' \\ S'' & 1/2 & S_2'' \end{Bmatrix}$$

$$\times \delta(l_1,t)\ (2l+1) \begin{pmatrix} l & l_1 & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \sum_{n_0 s}\ R^{l_1}(n_0 s\ nl, n_1 l_1 nl)\langle n_0 s|r^{-3}|n_2 s\rangle^{10}/\Delta E \Bigg]. \tag{21}$$

4.7.6 Configuration interaction $nl^N n_1 s \leftrightarrow nl^N n_2 l_2$

The states ψ for the $nl^N n_1 s$ configuration and ψ' for the $nl^N n_2 s$ configuration are defined as follows:

$$\psi = (n_0 s^2\ {}^1S, nl^N \alpha_1 S_1 L_1)\alpha_1 S_1 L_1, n_1 s; SL,$$

$$\psi' = (n_0 s^2\ {}^1S, nl^N \alpha_1' S_1' L_1')\alpha_1' S_1' L_1', n_2 l_2; S' L'.$$

For the excitation of an electron from a closed $n_0 s^2$ shell into an empty $n_1 s$ shell the perturbing virtual states are defined as $\psi'' = (n_0 s\ {}^2S, nl^N \alpha_1'' S_1'' L_1'')S'' L'', (n_2 l_2, n_1 s)S_2'' L_2''; S''' L'''$.

In this case the second term of the sum below is equal to zero due to hyperfine interaction (hfs operator is acting between electrons $n_0 s$ and $n_2 l_2$, radial integral $\langle n_0 s|r^{-3}|n_2 l_2\rangle^{10} \approx 0$):

$$-\sum_{\psi'' \neq \psi, \psi'} \left[\langle\psi|\mathbf{G}|\psi''\rangle \times \langle\psi''\|\mathbf{t^{10}}\|\psi'\rangle + \langle\psi\|\mathbf{t^{10}}\|\psi''\rangle \times \langle\psi''|\mathbf{G}|\psi'\rangle\right]/\Delta E. \tag{22}$$

The first component is as follows:

$$-\sum_{\psi''} \langle\psi|\mathbf{G}|\psi''\rangle \times \langle\psi''\|\mathbf{t^{10}}\|\psi'\rangle / \Delta E$$

$$= -\sum_{\psi''} \delta(\alpha_1' S_1' L_1', \alpha_1'' S_1'' L_1'')\ \delta(L, L')\ \delta(L_1', L'')\ [S, L, S', S'', S_2'']^{1/2}\ (-1)^{3S''+3S_1'+2S+1.5} \begin{Bmatrix} 1/2 & 1/2 & 1 \\ 1/2 & S_1' & S' \\ S_2'' & S'' & S \end{Bmatrix}$$

$$\times \Bigg[\sum_{\bar{\alpha}\bar{S}\bar{L}} N\ \delta(L'', L_1'')\ \delta(\bar{S}, S'')\ \left(nl^N \alpha_1'' S_1'' L_1'' \{|nl^{N-1}\bar{\alpha}\bar{S}\bar{L}\right)\ \left(nl^N \alpha_1 S_1 L_1 \{|nl^{N-1}\bar{\alpha}\bar{S}\bar{L}\right)$$

$$\times (-1)^{2S_1+3S''+S+\bar{L}+L_1+1}\ \frac{[S_1, S_1'', S_2'', L'']^{1/2}}{[S'']^{1/2}} \begin{Bmatrix} \bar{L} & l & L'' \\ l_2 & L_1 & l \end{Bmatrix} \begin{Bmatrix} 1/2 & S & S_1 \\ S'' & 1/2 & S_2'' \end{Bmatrix}$$

$$\times \delta(l,t)\ \sqrt{(2l+1)(2l_2+1)} \begin{pmatrix} l & l & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l & l_2 \\ 0 & 0 & 0 \end{pmatrix} \sum_{n_0 s}\ R^l(n_0 s\ nl, nln_2 l_2)\langle n_0 s|r^{-3}|n_1 s\rangle^{10}/\Delta E$$

$$+ \sum_{\bar{\alpha}\bar{S}\bar{L}} N\ \delta(L'', L_1'')\ \delta(S_1, S_1'')\ \left(nl^N \alpha_1'' S_1'' L_1'' \{|nl^{N-1}\bar{\alpha}\bar{S}\bar{L}\right)\ \left(nl^N \alpha_1 S_1 L_1 \{|nl^{N-1}\bar{\alpha}\bar{S}\bar{L}\right)$$

$$\times (-1)^{2S_1+3S''+S+\bar{L}+L_1}\ [S_2'', S'', L'']^{1/2} \begin{Bmatrix} \bar{L} & l & L'' \\ l_2 & L_1 & l \end{Bmatrix} \begin{Bmatrix} 1/2 & S & S_1 \\ S'' & 1/2 & S_2'' \end{Bmatrix}$$

$$\times \delta(l_2,t)\ (2l+1) \begin{pmatrix} l & l_2 & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & l_2 & 0 \\ 0 & 0 & 0 \end{pmatrix} \sum_{n_0 s}\ R^{l_2}(n_0 s\ nl, n_2 l_2 nl)\langle n_0 s|r^{-3}|n_1 s\rangle^{10}/\Delta E \Bigg]. \tag{23}$$

4.7.7 Configuration interaction $nl^N n_1 l_1 n_2 l_2 \leftrightarrow nl^N n_3 s\ n_2 l_2$

The states ψ for the $nl^N n_1 l_1 n_2 l_2$ configuration and ψ' for the $nl^N n_3 s\ n_2 l_2$ configuration are defined as follows:

$$\psi = (n_0 s^2\ {}^1S, nl^N \alpha_1 S_1 L_1)\alpha_1 S_1 L_1, (n_1 l_1, n_2 l_2) S_2 L_2; SL,$$

$$\psi' = (n_0 s^2\ {}^1S, nl^N \alpha_1' S_1' L_1')\alpha_1' S_1' L_1', (n_3 s, n_2 l_2) S_2' L_2'; S' L'.$$

For the excitation of an electron from a closed n_0s^2 shell into an empty n_3s shell the perturbing virtual states are defined as $\psi'' = [(n_0 s\ ^2S, nl^N \alpha_1'' S_1'' L_1'')S'' L'', (n_1 l_1, n_2 l_2) S_2'' L_2'']S_3'' L_3'', n_3 s; S''' L'''$.

In this case the first term of the sum below is equal to zero due to hyperfine interaction:

$$-\sum_{\psi'' \neq \psi, \psi'} \left[\langle \psi | \mathbf{G} | \psi'' \rangle \times \langle \psi'' \| \mathbf{t^{10}} \| \psi' \rangle + \langle \psi \| \mathbf{t^{10}} \| \psi'' \rangle \times \langle \psi'' | \mathbf{G} | \psi' \rangle \right] / \Delta E. \tag{24}$$

The second component is as follows:

$$\begin{aligned}
&-\sum_{\psi''} \langle \psi \| \mathbf{t^{10}} \| \psi'' \rangle \times \langle \psi'' | \mathbf{G} | \psi' \rangle / \ \Delta E \\
&= -\sum_{\psi''} \delta(\alpha_1 S_1 L_1, \alpha_1'' S_1'' L_1'')\ \delta(\alpha_1' S_1' L_1', \alpha_1'' S_1'' L_1'')\ \delta(S_2 L_2, S_2'' L_2'')\ \delta(L, L')\ \delta(L_1, L'') \\
&\times\ \delta(L, L_3'')\ \delta(L'', L_1')\ \delta(L', L_3'')\ \delta(L_2', l_2)\ \delta(L_2'', l_2)\ [S, L, S', S_2, S_2']^{1/2}\ [S'', S_3''] \\
&\times (-1)^{S+S'+L'+3S_1+3S_1'+S_2+S_2'+3S''+S_3''+L_1'} \begin{Bmatrix} 1/2 & S'' & S_1 \\ S_2 & S & S_3'' \end{Bmatrix} \begin{Bmatrix} S & S' & 1 \\ 1/2 & 1/2 & S_3'' \end{Bmatrix} \begin{Bmatrix} 1/2 & S_2' & 1/2 \\ S' & S_3'' & S_1' \end{Bmatrix} \begin{Bmatrix} 1/2 & S_1' & S'' \\ S_3'' & S_2'' & 1/2 \end{Bmatrix} \\
&\times \Bigg[\delta(l_1, t) \sqrt{2l_2 + 1} \begin{pmatrix} l_1 & l_1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & l_1 & l_2 \\ 0 & 0 & 0 \end{pmatrix} \sum_{n_0 s}\ R^{l_1}(n_0 s\ n_2 l_2, n_1 l_1 n_2 l_2) \langle n_0 s | r^{-3} | n_2 s \rangle^{10} / \Delta E \\
&+ \delta(l_2, t)\ (-1)^{S_2 + l_2} \sqrt{2l_1 + 1} \begin{pmatrix} l_1 & l_2 & l_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & l_2 & 0 \\ 0 & 0 & 0 \end{pmatrix} \sum_{n_0 s}\ R^{l_2}(n_0 s\ n_2 l_2, n_2 l_2 n_1 l_1) \langle n_0 s | r^{-3} | n_2 s \rangle^{10} / \Delta E \Bigg].
\end{aligned} \tag{25}$$

4.7.8 Configuration interaction $nl^N n_1 l_1^{N_1} \leftrightarrow nl^N n_1 l_1^{N_1 - 1} n_2 s$

The states ψ for the $nl^N n_1 l_1^{N_1}$ configuration and ψ' for the $nl^N n_1 l_1^{N_1 - 1} n_2 s$ configuration are defined as follows:

$$\begin{aligned}
\psi &= (n_0 s^2\ ^1S, nl^N \alpha_1 S_1 L_1) \alpha_1 S_1 L_1, n_1 l_1^{N_1} \alpha_2 S_2 L_2; SL, \\
\psi' &= (n_0 s^2\ ^1S, nl^N \alpha_1' S_1' L_1') \alpha_1' S_1' L_1', (n_1 l_1^{N_1 - 1} \alpha_2' S_2' L_2', n_2 s) S_3' L_3'; S' L'.
\end{aligned}$$

For the excitation of an electron from a closed n_0s^2 shell into an empty n_2s shell the perturbing virtual states are defined as $\psi'' = (n_0 s\ ^2S, nl^N \alpha_1'' S_1'' L_1'') S'' L'', (n_1 l_1^{N_1} \alpha_2'' S_2'' L_2'', n_2 s) S_3'' L_3''; S''' L'''$.

In this case the first term of the sum below is equal to zero due to hyperfine interaction:

$$-\sum_{\psi'' \neq \psi, \psi'} \left[\langle \psi | \mathbf{G} | \psi'' \rangle \times \langle \psi'' \| \mathbf{t^{10}} \| \psi' \rangle + \langle \psi \| \mathbf{t^{10}} \| \psi'' \rangle \times \langle \psi'' | \mathbf{G} | \psi' \rangle \right] / \Delta E. \tag{26}$$

The second component is as follows:

$$\begin{aligned}
&-\sum_{\psi''} \langle \psi \| \mathbf{t^{10}} \| \psi'' \rangle \times \langle \psi'' | \mathbf{G} | \psi' \rangle / \ \Delta E \\
&= -\sum_{\psi''}\ \delta(\alpha_1 S_1 L_1, \alpha_1'' S_1'' L_1'')\ \delta(\alpha_1' S_1' L_1', \alpha_1'' S_1'' L_1'')\ \delta(\alpha_2 S_2 L_2, \alpha_2'' S_2'' L_2'')\ \delta(L, L')\ \delta(L_1, L'')\ \delta(L_2'', L_3'') \\
&\times\ \delta(L_1', L'')\ \delta(L_3', L_3'')\ \delta(L_3', L_2'')\ \delta(L_2', L_2'')\ \delta(l_1, t)\ [S'', S_3'']\ \frac{[S, L, S', S_3', S_2]^{1/2}}{[L_2']^{1/2}} \\
&\times (-1)^{2S''+3S_1+S_2+2S_1'+2S_2'+S_3'+S_3''+S+2S'+1.5} \begin{Bmatrix} 1/2 & 1/2 & 1 \\ S_2 & S_1 & S \\ S_3'' & S'' & S' \end{Bmatrix} \begin{Bmatrix} S'' & 1/2 & S_1' \\ S_3' & S' & S_3'' \end{Bmatrix} \begin{Bmatrix} 1/2 & S_3'' & S_2'' \\ 1/2 & S_2' & S_3' \end{Bmatrix} \\
&\times \sum_{\bar{\alpha_2} \bar{S_2} \bar{L_2}} \sqrt{N_1}\ \delta(\bar{S_2}, S_2') \left(n_1 l_1^{N_1} \alpha_2'' S_2'' L_2'' \{ | n_1 l_1^{N_1 - 1} \bar{\alpha_2} \bar{S_2} \bar{L_2} \right)\ \left\langle n_1 l_1^{N_1 - 1} \bar{\alpha_2} \bar{S_2} \bar{L_2} \left\| \mathbf{U}^{l_1} \right\| n_1 l_1^{N_1 - 1} \alpha_2' S_2' L_2' \right\rangle \\
&\times (2l_1 + 1) \begin{pmatrix} l_1 & l_1 & l_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \sum_{n_0 s}\ R^{l_1}(n_0 s\ n_1 l_1, n_1 l_1 n_1 l_1) \langle n_0 s | r^{-3} | n_2 s \rangle^{10} / \Delta E.
\end{aligned} \tag{27}$$

4.7.9 Configuration interaction $nl^N n_1 l_1 n_2 s^2 \leftrightarrow nl^N n_1 l_1^2\ n_2 s$

The states ψ for the $nl^N n_1 l_1 n_2 s^2$ configuration and ψ' for the $nl^N n_1 l_1^2\ n_2 s$ configuration are defined as follows:

$$\psi = (n_0 s^2\ {}^1S, (nl^N \alpha_1 S_1 L_1, n_1 l_1) S_2 L_2) S_2 L_2, n_2 s^2\ {}^1S; SL,$$
$$\psi' = (n_0 s^2\ {}^1S, nl^N \alpha_1' S_1' L_1') \alpha_1' S_1' L_1', (n_1 l_1^2\ \alpha_2' S_2' L_2', n_2 s) S_3' L_3'; S' L'.$$

For the excitation of an electron from a closed $n_0 s^2$ shell into an open $n_1 l_1$ shell the perturbing virtual states are defined as $\psi'' = [n_0 s\ {}^2S, (nl^N \alpha_1'' S_1'' L_1'', n_1 l_1^2 \alpha_2'' S_2'' L_2'') S_4'' L_4''] S'' L'', n_0 s^2\ {}^1S; S''' L'''$.

In this case the second term of the sum below is equal to zero due to hyperfine interaction:

$$-\sum_{\psi'' \neq \psi, \psi'} \left[\langle \psi | \mathbf{G} | \psi'' \rangle \times \langle \psi'' \| \mathbf{t^{10}} \| \psi' \rangle + \langle \psi \| \mathbf{t^{10}} \| \psi'' \rangle \times \langle \psi'' | \mathbf{G} | \psi' \rangle \right] / \Delta E. \tag{28}$$

The first component is as follows:

$$\begin{aligned}
&-\sum_{\psi''} \langle \psi | \mathbf{G} | \psi'' \rangle \times \langle \psi'' \| \mathbf{t^{10}} \| \psi' \rangle / \ \Delta E \\
&= -\sum_{\psi''} \sqrt{2}\ \delta(\alpha_1 S_1 L_1, \alpha_1'' S_1'' L_1'')\ \delta(\alpha_1' S_1' L_1', \alpha_1'' S_1'' L_1'')\ \delta(S_2 L_2, S'' L'')\ \delta(SL, S'' L'')\ \delta(\alpha_2' S_2' L_2', \alpha_2'' S_2'' L_2'')\ \delta(L_4'', L'') \\
&\times \delta(L_2', L_3')\ \delta(l_1, t)\ [S_4'']\ [S, L, S', S_2', L_2', S_3']^{1/2} (-1)^{S_4''+S_1+S_1'+2S_2+2S_2'+L+S'+L'+L_2'+l_1+3/2} \begin{Bmatrix} 1/2 & S_2 & S_4'' \\ S_1 & S_2' & 1/2 \end{Bmatrix} \\
&\times \begin{Bmatrix} S & S' & 1 \\ 1/2 & 1/2 & S_4'' \end{Bmatrix} \begin{Bmatrix} S' & 1/2 & S_4'' \\ S_2' & S_1' & S_3' \end{Bmatrix} \begin{pmatrix} l_1 & l_1 & l_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \sum_{n_0 s}\ R^{l_1}(n_0 s\ n_1 l_1, n_1 l_1 n_1 l_1) \langle n_0 s | r^{-3} | n_2 s \rangle^{10} / \Delta E.
\end{aligned} \tag{29}$$

5 Results

In order to show the effectiveness of our method to a greater extent than was previously presented [30, 47, 48], we decided to choose lanthanum, as an atom with a complex structure and with a huge amount of experimental data concerning energy levels and hyperfine structure constants. Currently the La level list contains circa 430 even La I levels, all of them with known hyperfine constants A (in many cases also B constants are known). This allows an excellent test confirming the correctness of our method and mathematical formulae.

For the study of La, we considered the system of 100 even configurations:

$$\begin{aligned}
&4f^2 5d + 4f^2 6s + 4f5d5f + 4f5f6s + \sum_{n'=6}^{12} 4f5dn'p + \sum_{n'=6}^{12} 4f6sn'p + 5d^3 + \sum_{n'=6}^{15} 5d^2 n's + \sum_{n'=6}^{15} 5d^2 n'd \\
&+ \sum_{n'=5}^{14} 5d^2 n'g + 5d6s^2 + \sum_{n'=7}^{15} 5d6sn's + \sum_{n'=6}^{15} 5d6sn'd + \sum_{n'=5}^{14} 5d6sn'g + 5d6p^2 + 6s6p^2 + \sum_{n'=7}^{15} 6s^2 n's + \sum_{n'=6}^{15} 6s^2 n'd.
\end{aligned}$$

In our procedure we use all the experimental data known so far. A good agreement between experimental and calculated values of energy and hyperfine structure constants was achieved. The energy values and hfs constants for the levels up to approximately $45000\,\mathrm{cm}^{-1}$ were also predicted. Details of the analysis will be presented separately.

The examples of preliminary results of the semi-empirical fine and hyperfine structure analysis for La I are shown in table 1. The first two columns contain experimental and calculated level energies, respectively. In the subsequent four columns, the strongest and second strongest fine structure components with the corresponding percentages are presented. The comparison of calculated and experimental g_J values is presented in columns seven and eight. The experimental hyperfine constants A are listed together with their experimental uncertainty in column nine. The calculated A constants for all levels are given in column ten.

6 Conclusions

The present work on the hyperfine structure core-polarization effect is complementary to the previous five parts, that together describe all possible contributions originating from the second-order of the perturbation theory to the structure of complex atom.

Table 1. Comparison of the experimental and calculated energy values [cm^{-1}] and hfs A constants [MHz] for La I.

E_{exp}	E_{calc}	%	Main comp.	%	Sec. comp.	$g_{J_{calc}}$	$g_{J_{exp}}$	A_{exp}		A_{calc}
$J = 7/2$										
3494.525	3507	96.21	$5d^2(^3F)6s\ ^4F$	0.61	4f 5d6p (^3D) ^4F	1.238	1.237	462.868	(0.001)	457
8052.163	8056	86.48	$5d^2(^3F)6s\ ^2F$	4.94	$5d^3\ ^2F$	1.135	1.135	−197.064	(0.005)	−195
9960.904	9969	80.16	$5d^2(^1G)6s\ ^2G$	9.13	$5d^3\ ^2G$	0.898	0.892	−292.267	(0.005)	−305
13238.331	13241	97.26	$5d^3\ ^4F$	0.68	$4f^2(^3F)5d\ ^4F$	1.236	1.228	−19.103	(0.005)	−18
17023.342	17028	86.22	$5d^3\ ^2G$	8.48	$5d^2(^1G)6s\ ^2G$	0.892	0.880	162.3	(2.5)	151
21943.811	21937	86.21	$5d^3\ ^2F$	5.01	$5d^2(^3F)6s\ ^2F$	1.142		58	(37)	44
29045.820	29060	47.39	4f 6s6p (^3P) ^2F	24.95	4f 6s6p (^3P) ^4F	1.153	1.150	801.5	(0.5)	811
30055.037	30056	36.77	4f 6s6p (^3P) ^4F	22.00	$5d^2(^3F)7s\ ^4F$	1.173	1.190	374.9	(2.0)	349
30401.704	30409	60.54	4f 6s6p (^3P) ^4G	18.73	4f 6s6p (^3P) ^2F	1.040	1.030	365.3	(0.5)	303
31059.702	31082	56.97	$5d^2(^3F)7s\ ^4F$	17.50	4f 6s6p (^3P) ^4F	1.235	1.220	210	(1)	214
31287.605	31320	88.65	5d 6s7s (^3S) ^4D	2.65	$5d^2(^3F)6d\ ^4D$	1.419	1.410	805	(1)	812
31924.993	31873	47.72	4f 6s6p (^3P) ^4D	29.36	4f 6s6p (^3P) ^2G	1.227	1.270	513	(2)	501
32108.512	32113	67.84	$5d^2(^3F)7s\ ^2F$	9.21	$5d^2(^3F)7s\ ^4F$	1.141	1.130	−75	(5)	−58
32219.536	32199	42.45	4f 6s6p (^3P) ^2G	23.07	4f 6s6p (^3P) ^4D	1.100	1.060	160	(2)	191
33286.519	33268	41.31	$5d^2(^3F)6d\ ^4H$	16.57	$5d^2(^1D)6d\ ^2G$	0.801	0.780	283	(1)	247
33756.460	33698	49.98	$5d^2(^3F)6d\ ^4G$	13.51	$5d^2(^3F)6d\ ^2G$	0.994	0.990	167	(1)	191
...										
$J = 9/2$										
4121.572	4143	96.33	$5d^2(^3F)6s\ ^4F$	0.62	4f 5d6p (^3D) ^4F	1.333	1.333	489.534	(0.001)	495
9919.826	9914	83.65	$5d^2(^1G)6s\ ^2G$	8.17	$5d^3\ ^2G$	1.113	1.107	559.812	(0.005)	567
13747.276	13731	95.50	$5d^3\ ^4F$	1.96	$5d^3\ ^2G$	1.328		−63.829	(0.005)	−67
17140.940	17144	53.84	$5d^3\ ^2G$	34.83	$5d^3\ ^2H$	1.041		108.1	(5.3)	119
18315.822	18334	60.19	$5d^3\ ^2H$	32.56	$5d^3\ ^2G$	0.985	0.970	111.6	(2.6)	124
30409.369	30442	65.91	4f 6s6p (^3P) ^4F	19.55	$5d^2(^3F)7s\ ^4F$	1.322		584	(5)	566
30934.760	30931	73.55	4f 6s6p (^3P) ^4G	10.72	4f 6s6p (^3P) ^2G	1.166	1.158	605	(10)	630
31923.960	31870	73.97	$5d^2(^3F)7s\ ^4F$	13.71	4f 6s6p (^3P) ^4F	1.320	1.340	72	(5)	93
32448.352	32446	69.82	4f 6s6p (^3P) ^2G	8.24	4f 6s6p (^3P) ^4G	1.141		360	(3)	376
33753.424	33696	41.59	$5d^2(^3F)6d\ ^4H$	14.81	$5d^2(^1D)6d\ ^2G$	1.037	1.020	163	(2)	150
34526.709	34534	57.91	$5d^2(^3F)6d\ ^4G$	9.39	$5d^2(^3F)6d\ ^2G$	1.153		48	(1)	37
34635.015	34646	40.65	$5d^2(^3F)6d\ ^4H$	15.21	$5d^2(^1D)6d\ ^2G$	1.062	1.070	253.0	(2)	235
...										

We proved that it is possible to determine quantitatively the contributions of each interactions, and specify the precise definition of the evaluated parameters describing the interactions in the atom.

Our analyses clearly demonstrate that precise interpretation of the hyperfine structure is impossible without taking into account new parameters describing the contribution from electrostatic coupling with distance configurations, introduced in current work.

Presentation of precise definition of the parameters and explicit mathematical formulae allows to compare our approach with other theoretical methods of the description of atomic structure.

This work was supported by the Research Projects of the Polish Ministry of Sciences and Higher Education: 06/65/DSPB/0516 (ME) and 04/45/DSPB/0148 (JR and JD).

References

1. M. Elantkowska, J. Ruczkowski, J. Dembczyński, Eur. Phys. J. Plus **130**, 14 (2015).
2. M. Elantkowska, J. Ruczkowski, J. Dembczyński, Eur. Phys. J. Plus **130**, 15 (2015).
3. M. Elantkowska, J. Ruczkowski, J. Dembczyński, Eur. Phys. J. Plus **130**, 83 (2015).
4. M. Elantkowska, J. Ruczkowski, J. Dembczyński, Eur. Phys. J. Plus **130**, 170 (2015).
5. M. Elantkowska, J. Ruczkowski, J. Dembczyński, Eur. Phys. J. Plus **131**, 47 (2016).
6. R.E. Tress, Phys. Rev. **83**, 756 (1951).
7. R.E. Tress, Phys. Rev. **84**, 1089 (1951).
8. R.E. Tress, Phys. Rev. **85**, 382 (1952).
9. K. Rajnak, B.G. Wybourne, Phys. Rev. **132**, 280 (1963).
10. B.R. Judd, Phys. Rev. **141**, 4 (1966).
11. B.G. Wybourne, J. Math. Phys. **4**, 354 (1963).
12. B.G. Wybourne, *Spectroscopic Properties of Rare Earths* (Interscience, New York, 1965).
13. S. Feneuille, J. Phys. **28**, 61 (1967).
14. S. Feneuille, J. Phys. **28**, 315 (1967).
15. S. Feneuille, J. Phys. **28**, 497 (1967).
16. S. Feneuille, J. Phys. **28**, 701 (1967).
17. K. Rajnak, B.G. Wybourne, Phys. Rev. **134**, 596 (1964).
18. A. Pasternak, Z.B. Goldschmidt, Phys. Rev. A **1**, 55 (1972).
19. Z.B. Goldschmidt, J.V. Mallow, Phys. Rev. A **29**, 2401 (1984).
20. P.G.H. Sandars, J. Beck, Proc. R. Soc. A **289**, 97 (1965).
21. B.R. Judd, Proc. R. Soc. **82**, 874 (1963).
22. B.R. Judd, *La Structure Hyperfine Magnétigue des Atomes et des Molécules*, edited by R. Lefebvre, C. Moser (C.N.R.S., Paris, 1967) p. 311.
23. J. Bauche, B.R. Judd, Proc. Phys. Soc. **83**, 145 (1964).
24. P.G.H. Sandars, Adv. Chem. Phys. **14**, 365 (1969).
25. C. Bauche-Arnoult, Proc. R. Soc. A **322**, 361 (1971).
26. C. Bauche-Arnoult, J. Phys. **34**, 301 (1973).
27. L. Armstrong Jr., *Theory of the Hyperfine Structure of Free Atoms* (Willey-Interscience, New York, 1971).
28. I. Lindgren, A. Rosén, Case Stud. At. Phys. **4**, 93 (1974).
29. S. Büttgenbach, *Hyperfine Structure in 4d- and 5d-Shell Atoms* (Springer, Berlin, 1982).
30. J. Dembczyński, M. Elantkowska, B. Furmann, J. Ruczkowski, D. Stefańska, J. Phys. B: At. Mol. Opt. Phys. **43**, 065001 (2010).
31. J. Dembczyński, W. Ertmer, U. Johann, P. Unkel, Z. Phys. A **321**, 1 (1985).
32. J. Dembczyński, Physica C **141**, 219 (1986).
33. W. Ertmer, U. Johann, J. Dembczyński, Z. Michalski, Z. Phys. D **2**, 67 (1986).
34. R. Aydin *et al.*, Z. Phys. D **15**, 281 (1990).
35. J. Dembczyński, G.H. Guthoehrlein, E. Stachowska, Phys. Rev. A **48**, 2752 (1993).
36. J. Dembczyński, G. Szawioła, M. Elantkowska, E. Stachowska, J. Ruczkowski, Phys. Scr. **54**, 444 (1996).
37. M. Elantkowska, J. Ruczkowski, J. Dembczyński, Phys. Scr. **59**, 49 (1999).
38. J. Dembczyński, M. Elantkowska, K. Bekk, H. Rebel, M. Wilson, Z. Phys. D **13**, 181 (1989).
39. J. Dembczyński, Phys. Scr. **T65**, 88 (1996).
40. J. Dembczyński *et al.*, Hyperfine Interact. **127**, 49 (2000).
41. J. Bauche, C. Bauche-Arnoult, J. Phys. B **10**, L125 (1977).
42. G. Himmel, Z. Phys. **211**, 68 (1968).
43. U. Johann, J. Dembczyński, W. Ertmer, Z. Phys. A **303**, 7 (1981).
44. G. Racah, Phys. Rev. **63**, 367 (1943).
45. G. Racah, Phys. Rev. **76**, 1352 (1949).
46. V.L. Donlan, J. Chem. Phys. **52**, 3431 (1970).
47. J. Dembczyński, M. Elantkowska, J. Ruczkowski, I.K. Öztürk, A. Er, F. Güzelçimen, Gö. Başar, S. Kröger, J. Phys. B: At. Mol. Opt. Phys. **48**, 015006 (2015).
48. J. Dembczyński, M. Elantkowska, J. Ruczkowski, Phys. Rev. A **92**, 012519 (2015).